DECLARATION OF YUICHIRO SHINDO
UNDER 37 CFR §1.132

I, Yuichiro Shindo, having been wanted in accordance with Section 1001 of Title 18 of the United States Code, declare that: I have 20 years of experience in the research and development of sputtering target materials and my educational degrees include:

I am an inventor of the present invention. I will explain the differences in the manufacturing method, structure and characteristics of the target between the present invention and Document 1 (U.S. Patent No. 6,861,030 B2).

(Technology of Document D1 (U.S. Patent No. 6,861,030))

I am also the inventor of the invention of Document D1. Document D1 is an invention related to the method of producing high purity Zr or Hf. Moreover, by hydrogenating the high purity Zr or Hf and thereafter heating this in a vacuum or an inert atmosphere to eliminate hydrogen, high purity Zr powder or Hf powder can also be produced. In addition, by sintering this powder, a high purity Zr or Hf sputtering target can also be produced.

The primary objective of the invention of Document D1 is to inexpensively produce high purity Zr and Hf upon distinctly reducing impeditive impurities in order to guarantee the operating performance of semiconductors, whereby the foregoing impurities include alkali metal elements such as Na, K, radioactive elements such as U and Th, transition metals such as Fe, Ni, Co, Cr, Cu, Mo, Ta, and V, heavy metal or high melting point metal, and even gas components such as C and O.

Thus, in order to inexpensively produce high purity Zr or Hf, Document D1 cleans commercial available Zr or Hf sponge raw material having a purity level of 2 to 3N using fluoric acid, eliminates contaminants such as organic matter or inorganic matter that adhered to the raw material surface, and additionally refines this by way of EB melting so as to produce high purity Zr and Hf in which the impurity content excluding gas components such as C and O is less than 100ppm.

The production method of high purity Zr and Hf of Document D1 employs fluoric acid cleaning and EB melting, but these methods are unable to intentionally eliminate Hf and Zr as impurities. The reason for this is because both elements are homologous elements and have very similar physical properties. Thus, it is extremely difficult to separate and refine Hf and Zr only with fluoric acid cleaning and electron beam melting.

Here, as additional testing, when Hf raw material having a Zr content of 1 to 1000ppm (600ppm, 700ppm, etc.) was processed with the same method as Document D1 (acid cleaning and EB melting), the Zr content in Hf did not change. Moreover, with the temperature of 2300ºC (2573K) during the EB melting, the vapor pressure was approximately fixed at 4.0×10^{-3} torr. In other words, since there is hardly any difference in the vapor

pressure at the temperature during the EB melting, it would be impossible for only Zr to decrease based on EB melting.

Incidentally, although the Zr content decreased from 25000ppm to 3500ppm after the fluoric acid cleaning and electron beam melting in Document D1, this is a result of Zr that was adhered to the surface being eliminated due to acid cleaning. Thus, if the Zr content is low to begin with as in the present case, Zr will not be adhered to the surface and, therefore, will not be eliminated by way of acid cleaning.

(Technology of Present Invention)

Meanwhile, the present invention relates to a method of producing a high purity Hf ingot in which the Zr content contained in Hf is reduced. Moreover, a high purity Hf sputtering target can also be produced from the foregoing high purity Hf ingot. The primary objective of the present invention is to separate and refine Zr, which has a very similar atom structure and chemical properties as Hf, from Hf, and to stabilize the characteristics of the electronic components employing Hf in which the Zr content contained in Hf is reduced.

Thus, the present invention dissolves commercially available Hf tetrachloride raw material ($HfCl_4$) in purified water, and thereafter performs multistage organic solvent extraction to make Zr 1000wtppm or less. Subsequently, neutralization treatment is performed to achieve HfO_2, and this is chlorinated to achieve high purity Hf tetrachloride ($HfCl_4$). Then this high purity Hf tetrachloride is reduced using reducing metal such as magnesium metal to prepare a high purity Hf sponge. This is further refined with electron beam melting to produce high purity Hf in which Zr is 1 to 1000wtppm, and the purity excluding gas components such as C, O and N is 4N (99.99wt%) or higher.

By adopting the method provided by the present invention, Zr as an impurity can be effectively eliminated from Hf. Moreover, a high purity sputtering target can be directly obtained from a high purity sputtering target that was obtained by performing electron beam melting to the Hf sponge in which the Zr content was reduced. As a result of using the high purity sputtering target manufactured as described above, characteristics of the semiconductor thin film formed from hafnium silicide or the like can be stably maintained. It is evident that the method of the present invention for producing a high purity Hf ingot in which the Zr content contained in Hf is reduced yields numerous advantages.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like are punishable by fine and imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Date: 2009/06/24

Yuichiro Shindo

Signature: Yuichiro Shindo